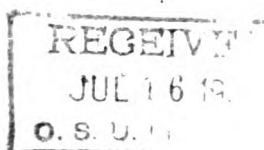


UNITED STATES BUREAU OF MINES
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GREENSAND



BY

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Foreword

The enormous deposits of greensand in New Jersey and elsewhere in the United States, many of them close to important industrial centers, constitute a perpetual challenge for research chemists to convert them into a commercial asset of national importance. Following the introduction of more concentrated fertilizers, comprising synthetic mixtures of more soluble salts, the quantity of greensand used directly upon the soil has diminished, but deposits of such material still have at least potential value locally for use not only as fertilizer but also as a water softener.

An annotated bibliography of the already extensive literature on greensand, virtually complete to about the end of 1929, has been issued by the Bureau of Mines^{3/}, and the commercial aspects as well as the technology of greensand utilization are discussed in available publications. The purpose of the present circular, therefore, is merely to provide a brief outline of certain general essential considerations for use in appraising the potential value of a greensand deposit in any given locality.

Description

The term "greensand" is applied to an unconsolidated or sandy deposit containing glauconite, a hydrous silicate of iron and potassium. It may contain less than 1 percent of quartz sand; but more commonly it contains a much larger amount of inert material, often 50 percent or more. Sand composed mainly of glauconite is distinctly green, becoming darker or even almost black when wet. If much quartz is present the sand has a characteristic "pepper-and-salt" appearance. Fresh glauconite is green but after being weathered takes on a dark coating. The grains of glauconite are fairly soft and can be broken readily by the finger nail.

^{1/} The Bureau of Mines will welcome reprinting of this article, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6782."

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^{3/} Sireve, R. M., Greensand Bibliography to 1930 (Annotated), with a chapter on Zeolite Water Softeners: Bull. 328, Bureau of Mines, 1930, 78 pp.

In addition to glauconite and quartz, many greensand deposits contain calcium carbonate (usually as shells or as cement derived from shells) and a little clay or other fine material. Some deposits contain more or less phosphate of iron. Undecayed feldspar is found occasionally, and in many southern deposits there is an appreciable amount of mica.

Glauconite (from the Greek word *glaukos*, meaning bluish green) is a definite mineral, as shown by its X-ray patterns, but samples from different localities vary considerably in analysis. In general, however, it consists of about one half silica, one fourth iron oxides, one tenth aluminum and magnesium oxides, and one sixth potash, water, and other substances, the potash forming about 1 part in 13. Inasmuch as pure glauconite contains about 7 to 8 percent potash the potash content of a greensand often can be estimated roughly on the basis of its glauconite content, but departures from this rule frequently are noted. The best New Jersey greensands contain up to 7 percent or more of potash, analyses ranging from 1.54 to 7.15 K₂O, with 0.19 to 6.9 percent P₂O₅.

Greensand deposits frequently are described as "marls"; this usage is firmly established in geologic reports as well as popular speech, but the term "marl" is applied accurately only to earthy deposits containing an appreciable amount of lime (calcareous marls).

The specific gravity of glauconite usually is given as around 2.3, although selected samples of New Jersey greensand have shown a density of around 3.0. Mansfield⁴ estimated the average weight of the material as 80 pounds per cubic foot or 3,160 pounds per cubic yard when stored in stock piles and at 133 pounds or about 3,580 pounds per cubic yard in place.

Allied to glauconite and greensand in composition are the so-called "green earths", which occur as alteration products of basic igneous rocks. The well-known "green-earth" pigment of Monte Baldo and elsewhere near Verona, Italy, is celadonite, a mineral which is perhaps identical with glauconite, differing only in its state of aggregation and origin.

Greenalite also resembles glauconite, both in general appearance and composition; it is a hydrated iron silicate but contains no potash.

Uses

Inasmuch as the New Jersey greensand contains both potassium and phosphorus, 2 of the 3 principal elements essential to the growth of plants, "marl" was used as a fertilizer in that State as early as 1763, though not abundantly until about 1820. As much as 200 loads per acre sometimes were used, and such dressings were deemed sufficient to last 15 or 20 years. Various annual reports of the New Jersey Geological Survey record the use of 5 to 50 tons or more spread after sowing. The crops most benefitted were

⁴/ Mansfield, G. R., Potash in the Greensands of New Jersey: U. S. Geol. Survey Bull. 727, 1922, p. 20.

grass, clover, potatoes, and buckwheat; but all grains were said to be improved, though with less striking results. Even modern agricultural chemists seem to be more or less in agreement as to the value of greensand as a fertilizer. It must be used in relatively large quantities, however, as its potash is only slowly soluble. The addition of ground limestone with certain greensands is recommended. Because of the large quantities required, greensand has rarely been used in the United States outside of New Jersey for direct application to the soil. In Virginia, however, considerable tonnages have been dried and ground for use in commercial fertilizers.

Greensand has been considered repeatedly as a potential source of soluble potash salts. Thoenen⁵ reported in 1929 that no large-scale successful process was in operation, and he concluded that expansion of existing experimental processes to supply domestic potash needs would encounter difficulties in marketing byproducts (chiefly sand-lime brick or synthetic portland-cement slurry). However, he recommended further laboratory study and glimpsed an opportunity for one or more moderately large plants utilizing this material in New Jersey. Later developments, notably the large prospective increase in the domestic potash production from New Mexico, do not tend to improve the potential competitive status of greensand as a source of soluble potash salts. During the World War a large potash-recovery plant was under construction near New Brunswick, N. J., but it was never completed, and its costly equipment remained idle or was subsequently sold for other purposes. The design called for the manufacture of sand-lime brick as a byproduct.

In recent years most of the rather small annual production of greensand is treated and sold for use in water-softening apparatus, relatively little now being employed as fertilizer. Inasmuch as this is now the principal use it will be discussed in some detail, along with competing synthetic zeolites in the section of this paper on Water Softening.

Greensands have been used occasionally, probably in only a small way, in the ceramic industry, for preparing special slips and ceramic bodies.

Mode of Occurrence

Glaucinite has formed in every geologic age since pre-Cambrian times, and even in older rocks the related mineral, greenalite, is found. According to Ashley⁶, the unconsolidated greensands of the North Atlantic States occur as well-defined beds in the Aquia and Shark River formations of the Eocene and in the Manasquan, Rancocas, and Monmouth formations of the Cretaceous. At present glauconite is one of the important materials forming on the bottom of the sea at depths ranging from about 300 feet to a little over 2 miles.

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- 5/ Thoenen, J.R., Potash from New Jersey Greensand - Preliminary Report: Rept. of Investigations 2910, Bureau of Mines, 1929, 54 pp.
 6/ Ashley, G. H., Notes on the Greensand Deposits of the Eastern United States: U. S. Geol. Survey Bull. 660, 1918, p. 36.

According to the report of the Challenger expedition,^{7/} it forms most abundantly at about the lower limits of wave, tide, and current action, in the neighborhood of what may be called the mud line--that is, at about 200 to 300 fathoms.

A great deal has been written about the origin of glauconite. Many writers ascribe the formation of the material to the action of decaying animal matter in the sea, while others call attention to the fact that it may be formed in existing sediments by percolating waters, both by direct precipitation from solution and by replacement of pre-existing minerals.

Distribution of Deposits

In the United States greensand occurs in New Jersey, Delaware, Maryland, Virginia, North Carolina, Tennessee, Texas, and Arkansas. In England it is developed in the Walsden area and on the Isle of Wight, and extends from Berkshire and Oxfordshire to Norfolk and Lincolnshire. Some of the limonite iron ores of these districts may, like those of the Lake Superior region, have been derived by alteration of glauconite.^{8/} The same formation is distributed widely on the continent of Europe.

The greensand beds of New Jersey alone probably contain over 2 billion metric tons in a belt 10 miles wide and 100 miles long, and averaging 20 feet thick.^{9/} Mansfield^{10/} estimates that a triangular prism 2.1 miles wide, 100 miles long, and 40 feet thick at the southeast border (wedging out along its northwesterly border) can be mined by open-pit methods. Even with due allowance for erosion and disregarding land already developed for residential and industrial purposes the potential tonnage in this area is enormous. If the potash content, for example, were available, this area could supply the probable potash needs of the United States for centuries.

Most of the deposits south of Delaware appear to be of lower grade than the New Jersey greensand. According to Ashley^{11/}, samples from New Jersey and Delaware yielded as much as 7 percent and more of potash; samples from Maryland yielded 4.45 percent or less; samples from Virginia, which contained much lime, yielded 3 to 2.5 percent; those from North Carolina 2.96 percent or less; those from Arkansas 4.9 percent or less; and a sample from Tennessee not over 3 percent.

^{7/} Murray, J., and Renard, A. F., Challenger Report, Deep-Sea Deposits: 1891, p. 383, Diagram 2. (Quoted by Mansfield, G. R., Work cited, p. 138.)

^{8/} Thorpe, E., A Dictionary of Applied Chemistry: Vol. III, p. 402.

^{9/} Washington, H. S., Italian Leucite Lavas as a Source of Potash: Met. and Chem. Eng., vol. 18, 1918, p. 71.

^{10/} Mansfield, G. R., Work cited, p. 106.

^{11/} Ashley, G. H., Work cited, p. 29.

Mining

The bulk of the greensand produced in the United States has come from small, hand-pick-and-shovel operations. For the New Jersey deposits, Thoenen^{12/} visualizes no particular difficulties in removing overburden by dragline and mining the greensand by dragline or dredging operations. He assumes an average ratio of overburden of 1 cubic yard for each 4.1 tons of greensand and a cost of 15 cents for stripping and 30 cents for mining per cubic yard of greensand, or 24 cents per ton, exclusive of freight to the treatment plant.

Domestic Production

In the late 1860's almost a million tons of greensand were dug and used as fertilizer every year.^{13/} Even before the Civil War hundreds of thousands of bushels were shipped locally to New Jersey farms. In 1855 it was worth 7 cents a bushel, and in 1877 it was selling as low as 60 cents a ton at the pits, with freight for a 25-mile haul bringing the delivered cost in many cases up to \$1.15. Much of the output was dug by farmers in the "marl" districts and used near by; but considerable quantities were hauled some distance by wagons, and in the aggregate thousands of carloads were shipped by rail, the railroad companies often building spur tracks directly into the pits. These fragmentary data from various reports indicate a highly prosperous industry, with gross receipts eventually exceeding \$800,000 a year from a relatively small section of the country. By the seventies the heyday of the industry seems to have passed; but in 1873, 134,734 tons were reported as shipped and an equal amount as dug by farmers for their own use. In 1878, only 39,918 tons were shipped, but in 1881, 8 companies shipped a total of 73,900 tons. This seems to have been followed by a lull until about 1897, when signs of a revival were reported. In 1900, the production, including a small quantity from Virginia, was 90,930 tons valued at \$124,830, but this improvement was only temporary. In 1908 the output had dropped to 8,246 tons valued at \$3,416; continuing the decline only 314 tons valued at \$223 were produced in 1913. From 13 operators in 1908 the number dropped to 4 in 1912 and 1913, and throughout this period the product was mostly dug by owners of the pits for their own use. The wartime shortage of potash occasioned only a relatively small increase to a maximum of 3,582 tons valued at \$4,775 in 1918.

The use of greensand for water-softening brought about a revival in the industry; and in 1922, 4 operators reported a production of 7,835 tons valued at \$56,800, equivalent to more than \$7 a ton. In the following year the average was over \$13 a ton. The high unit value is noteworthy compared with the price of under \$1 a ton placed upon the crude material for use as fertilizer.

^{12/} Thoenen, J. R., Work cited.

^{13/} Cook, G. H., Geology of New Jersey: 1866, p. 461. (Quoted by Mansfield, G. R., Work cited, p. 1.)

Available production data for recent years are shown in an accompanying table.

Table 1. - Production of greensand in New Jersey, 1922-30 1/

Year	Plants	Short tons	Value	Year	Plants	Short tons	Value
1922	4	7,885	\$ 56,800	1927	5	11,259	\$163,048
1923	4	10,656	131,123	1928	5	12,295	209,047
1924	4	14,055	151,205	1929	5	13,016	253,180
1925	5	12,728	179,788	1930	5	12,761	224,871
1926	5	12,606	174,365				

1/ The Mineral Industry of New Jersey (Annual).

In 1930 the plant of one company, Potash-Marl (Inc.), near Marlton, was sold and dismantled, but in that year a new plant was opened up near Sewell by the Inversand Co. at Clayton. The present list of operators includes the following:

The Permutit Co. (Birmingham, N. J.), 440 Fourth Ave., New York, N. Y.
Zeolite Chemical Co. (Reeves Station, N. J.), 90 West St.,
New York, N. Y.

Marl Mining Corporation, Office, Pit, and Plant at Marlton, N. J.
Hoffman & Caps Chemical Co. (Evansville, N. J.), Box 586,
Mount Holly, N. J.

The Inversand Co. (Sewell, N. J.), Clayton, N. J.

Imports and Exports

Greensand is not separately classified in either the import or the export schedules of the Department of Commerce but it is reasonable to assume that the material is much too bulky to enter largely into international trade. Undoubtedly some quantity of greensand, more or less advanced in condition or manufactured, has been included in the exports of mixed fertilizers and prepared water softeners.

Zeolite Water Softening

The "hardness" of water has an important bearing on its industrial utilization. Calcium carbonate held in solution by carbon dioxide imparts what is known as temporary hardness, inasmuch as it is virtually removable by heating to the point where the gaseous carbon dioxide is expelled; it is likewise precipitated by adding milk of lime. So-called permanent hardness, due to calcium sulphate, may be largely removed by adding soda ash. Various chemical and other treatments have been used for many decades to prevent boiler scale; but even when solids are removed by preliminary filtering the boilers had to be blown, usually at least once a day, to prevent

priming and other difficulties arising from the introduction of soluble salts, usually in considerable excess of the minimum required for the removal of scale-forming elements.

The advantages of completely softened water, essentially free from both calcium and magnesium (zero hardness), are manifold. In steam power plants and even in large heating plants it eliminates formation of scale in boilers, feed pumps, feed pipes, and the circulating system in general, thereby saving a great deal of unnecessary expense for fuel, repairs, and maintenance. In laundries softened water saves soap and does better work; and in textile mills, chemical works, and a great variety of industrial establishments it cuts costs and improves the quality of the product. Data showing the loss of efficiency due to scale and methods for treating boiler water are described in Bureau of Mines Technical Paper 218, *Boiler-Water Treatment*, by the United States Fuel Administration (1919). The magnitude of the industries concerned in supplying chemicals and apparatus for water softening is indicated in an article in *Commerce Reports* of September 28, 1931 (pp. 779-781), which shows that the domestic production of boiler compounds was valued at \$5,867,285 in 1927 (\$4,904,866 in 1929) and sales of small automatic household water-softening apparatus amounting to 16,189 units valued at \$1,903,587 in 1928 (declining to 11,783 units valued at \$1,495,247 in 1930). Unofficial estimates place the quantity of aluminum sulphate used annually for water treatment at 200,000 tons and soda ash in excess of 100,000 tons. Other water-treatment chemicals include lime-barium carbonate, witherite (natural barium carbonate), barium carbonate, sodium and barium aluminates, ferric alumina, sulphur dioxide, sodium silicate, ammonia, copper sulphate, chlorine, ferrous sulphate (copperas), and the important group of zeolites or sodium aluminum silicates.

The principle of zeolite water softening is that of base exchange. The calcium and magnesium salt in the raw water is replaced by the corresponding sodium salt when the water comes in contact with the zeolite, which in turn becomes depleted in sodium and correspondingly saturated with calcium and magnesium. The process is reversible, however, and the exhausted mineral is readily regenerated when a strong solution of sodium chloride (common salt) is passed through it; the preponderance of sodium causes a reverse change replacing the calcium and magnesium stored in the mineral and allowing them to be washed away as chlorides.

The base-exchange properties of zeolites were noted as early as 1850 and by 1896 were utilized in beet-sugar refining, but it was not until the twentieth century that they were utilized for water softening.^{14/} The earlier types of zeolites were made by fusing appropriate raw materials but were slow acting, requiring 8 to 12 hours of contact. Later, bentonitic clays were found which were somewhat more satisfactory. The use of New Jersey greensand came next, resulting in greatly accelerated water-softening

^{14/} Behrman, A. S., *Early History of Zeolites: Jour. Am. Water Works Assoc.*, vol. 13, no. 2, 1925, pp. 221-225.

rates and much more rapid regeneration. Of still later development were synthetic zeolites, which are claimed to be superior even to the natural greensands; one of the most recent is made by mixing solutions of sodium silicate and aluminum sulphate in proper proportions, forming a stiff homogeneous gel.^{15/}

It will be noted that greensand is by no means alone in its field, but the production figures on page 6 indicate that the New Jersey industry is just about holding its own. The field of water softening is definitely expanding, especially in combination with a preliminary treatment with lime. Often a portion of the total water can be passed through the zeolite system and still produce a mixture of water of the desired degree of softness.

^{15/} Behrman, A. S., Recent Developments in Zeolite Softening: Ind. and Eng. Chem., vol. 19, no. 4, 1927, p. 446.